Tetrahedron Letters Vol. 22, pp 173 - 176

0040-4039/81/0108-0173$02.00/0

TETRAMETHYLCYCLOBUTADIENE RADICAL CATION

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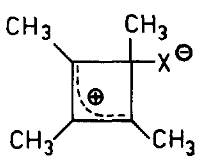
Summary: The tetramethylcyclobutadiene radical cation has been generated photochemically in solutions of aluminum halide σ complexes of tetramethylcyclobutadiene. It decays thermally to a "dimeric" radical cation.

The chemistry of aluminum halide σ complexes of alkyl-substituted cyclobutadienes has been shown useful in the synthesis of a variety of mono- and bicyclic compounds.[1] The intramolecular mobility of the $AlCl_3$-group in these complexes involves rapid 1,2 shifts along the cyclobutadiene ring.[1a] In the present communication preliminary results are presented that indicate that low-temperature photolysis of e.g. complex 1a or 1b leads to homolysis of the carbon aluminum bond affording the corresponding radical cation of tetramethyl cyclobutadiene. In addition, thermal decay at low temperatures of this radical cation has been detected to afford a "dimeric" radical cation.[2] Very recently, Maier and coworkers[3] reported the



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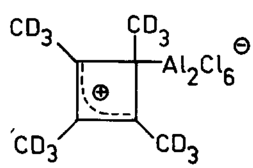
1a X=$AlCl_3$

1b X=Al_2Cl_6

1c X=Al_2Br_6



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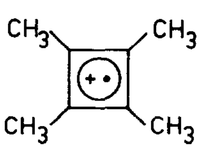

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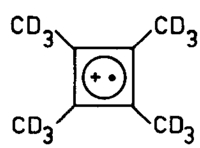

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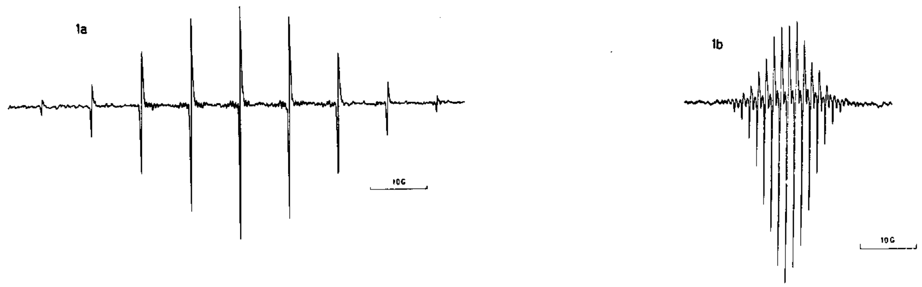


Fig. 1: ESR spectra of radical cation 3 (Fig. 1a) and 4 (Fig. 1b) at $-80^{o}C$

tetra tert.-butylcyclobutadiene radical cation, using $AlCl_3/CH_2Cl_2$ as oxidizing agent on either the corresponding tetrahedrane or cyclobutadiene.

When a 0.5 molar solution of either complex 1a or 1b[4] was irradiated at $-80^{o}C$ in the ESR cavity[5] with a Philips SP 500 UV lamp, the ESR spectrum, shown in Fig. 1a, and ascribed to radical cation 3, appeared (g-value: 2.0030; 11 of the expected 13 lines have been observed). The line intensities of the spectrum agree with a coupling of the electron spin with 12 identical hydrogen atoms, a^H being 8.75 G. The radical cation 4 (Fig. 1b) is similarly obtained in CD_2Cl_2 or CH_2Cl_2 solution from complex 2, the coupling constant a^D being 1.32 G, which is in agreement with the theoretically expected value ($a^D = \frac{a^H \mu_D I_H}{\mu_H I_D} = 1.34$ G).

When the lamp is switched off, the ESR spectrum of 3 decreases in intensity and a much more complicated spectrum appears[6] (Fig. 2) (g-value: 2.0030). The stability of the radical cation responsible for this spectrum is strongly determined by the presence of oxygen in the system. The identical spectrum is obtained on reaction of octamethyl-syn-tricyclo-$[4.2.0.0^{2,5}]$-octadiene with $AlCl_3$ in CH_2Cl_2 at room temperature. The computer simulated spectrum[7]

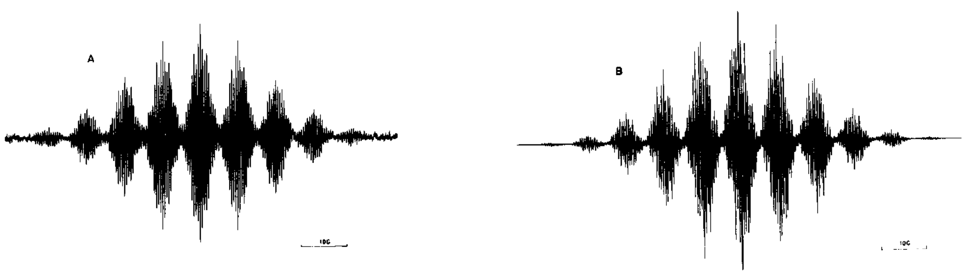
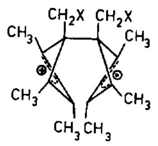


Fig. 2: Experimental (A) and computer-simulated (B) ESR spectra of the "dimeric" radical cation.

was obtained using for the hyperfine coupling constants the following values: a_1^H (12H): 8.37 G, a_2^H (6H): 1.38 G, and a_3^H (4H): 0.46 G (line width: 0.18 G). The structure of this radical cation, which might be formed by oxidative dimerization of 3, is not yet known but may be either 5[8] (in which a rapid electron transfer between the two cyclobutenyl ring systems occurs, X being unknown) or 6.



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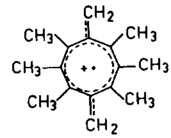

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It is of interest to speculate about the antiaromatic character of the cyclobutadiene radical cations 3 and 4. Ilič and Trinajstič[9] have very recently applied the method of topological resonance energy (TRE) to many conjugated species, including the cyclopropenyl radical and the cyclobutadiene radical cation: the destabilization in terms of TRE per π electron is virtually the same (-0.155 and -0.154, respectively).

Comparison of the enthalpies of formation of cyclobutane, cyclobutene and cyclobutadiene with those of the corresponding radical cations show that the destabilization of the cyclobutadiene radical cation is only half of that of cyclobutadiene on linear extrapolation from cyclobutane to cyclobutene to cyclobutadiene.[10]

The relatively high antiaromatic character of the cyclopropenyl radical has been calculated by Hess and Schaad[11] and suggested to be in agreement with experimental data. Whether the destabilizing effect of alkyl groups on cyclopropenyl radicals[12] is also valid for cyclobutadiene radical cations remains uncertain without further experimental data. We are at present engaged in establishing to what extent the aluminum halide σ complexes of substituted cyclobutadienes can be exploited in generating the corresponding radical cations.

Acknowledgment: The authors wish to thank Professors I. Agranat, E. Heilbronner and G. Maier for correspondence and discussions on the subject.

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c. H. Hogeveen and D.M. Kok, manuscript in preparation for "Supplement C. The Chemistry of Triple-Bonded Groups" (Ed. by S. Patai and Z. Rappoport).

2. For leading references on radical cations see G. Vincow in "Radical Cations", Ed. E.T. Kaiser and G. Kevan, Interscience Publishers, 1968, Chapter 4; A.J. Bard, A. Ledwith and H.J. Shine, Adv. Phys. Org. Chem., 13, 155 (1976).

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4. The solutions of the complexes were prepared by degassing a solution of 2-butyne in CH_2Cl_2 and a suspension of $AlCl_3$ in CH_2Cl_2 by several freeze-thaw cycles and a pressure not exceeding 10^{-5} Torr. Thereafter the solutions were combined at liquid nitrogen temperature, the tubes sealed and warmed up to room temperature. These solutions already contained the blue-green coloured "dimeric" radical cation which is persistent for several days. For the irradiation experiments solutions of the complexes were used from which the "dimeric" radical cation had vanished.

5. The ESR spectra were recorded on a Varian E-4 apparatus equipped with a Varian A-1268 variable temperature controller. Temperatures were measured with a Cu-Const. thermocouple.

6. At room temperature identical spectra were obtained using $CHCl_2CHCl_2$ as solvent for 1b and CH_2Br_2 for 1c.

7. The simulation program was kindly provided by Dr. J.H. Lichtenbelt, Department of Chemistry, this University.

8. Structure 5 is reminiscent of the dication obtained on reaction of octamethyl-syn-tricyclo[4.2.0.0^{2,5}]octadiene with SbF_5; G.A. Olah, G. Liang, L.A. Paquette and W.P. Melega, J. Am. Chem. Soc., 98, 4328 (1976).

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(Received in UK 24 October 1980)